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MOLECULAR SPECTRAL INTERFERENCE IN THE DETERMINATION OF ARSENIC BY FURNACE ATOMIC ABSORPTION

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ABSTRACT

A molecular spectral interference associated with a certain type of suspended particulate matter in natural waters is reported for the furnace atomic absorption determination of arsenic. In some water samples, arsenic concentrations were erroneously high by more than a factor of five above the actual concentration. Results of analyses were confirmed by an alternate analytical method. The degree of interference is a function of spectral bandpass and the concentration of hydrofluoric acid added to the sample. Use of a 0.2 nm bandpass or 1% hydrofluoric acid markedly reduced the interference for the natural water samples investigated.

RESUME

On a constaté une interférence spectrale moléculaire provoquée par certaines particules suspendues dans des eaux naturelles lors du dosage de l'arsenic par absorption atomique avec four. Pour certains échantillons d'eau, les teneurs d'arsenic avaient une erreur par excès d'un facteur cinq par rapport aux concentration réelles.
Les résultats des analyses ont été confirmées par ceux d'une méthode analytique différente. Le degré d'interférence, en fonction de la bande spectrale et de la concentration en acide fluorhydrique ajoutée à l'échantillon.
Le choix d'une bande passante de 0.2 nm et une concentration de 1% d'acide fluorhydrique ont permis d'atténuer nettement l'interférence pour les eaux naturelles étudiées.

ZUSAMMENFASSUNG

Es wird in Zusammenhang mit der Bestimmung von Arsen mittels Atom Absorptions Spektroskopie und Graphitrohrküvette über molekulare spektrale Interferenzen, welche im Zusammenhang mit einigen suspendierten Schwebestoffen in natürlichen Wässern auftreten, berichtet. In einigen Wasserproben waren die erhaltenen Arsen-Konzentrationen fälschlicherweise um mehr als den Faktor 5 über den tatsächlichen Konzentrationen. Die Analysenresultate wurden durch andere analytische Methoden bestätigt. Der Grad der Interferenz ist eine Funktion der spektralen Spaltbreite und der Flussäure Konzentration, die der Probe zugefügt wird. Die Verwendung einer Spaltbreite von 0.2 nm und eine einprozentige Flussäure Konzentration reduzierten die Interferenzerscheinung bei den untersuchten natürlichen Wasserproben beträchtlich.

INTRODUCTION

Previous studies have suggested that measurements of arsenic by Graphite Furnace atomic absorption may a significant role in environmental trace analysis (1, 2). Although previous workers have investigated possible interferences in the method due to other cations and anions (3, 4), little is known about the type of interference, particularly from suspended particulate matter in natural water samples. The objective of this paper is to report the observation of a spectral-type interference that was associated with suspended natural particulate matter high in silica content. A possible solution to the problem is suggested.

EXPERIMENTAL

Aliquots (15 ml) of acidified (0.2% v/v HNO_3, Baker Ultrex*) natural water samples and 0.15 ml of reagent-grade hydrofluoric acid (Mallinckrodt, 48%) were placed in Teflon-lined pressure decomposition vessels (Parr) and digested at 140°C for 5 hr to solubilize particulate matter. This procedure resulted in a highly transparent colorless solution, and turbidity measurements with a Hach Model 2103A turbidimeter indicated that a water sample originally as high as 110 NTU was reduced to 2.1 NTU after digestion. Routine recovery experiments on natural samples indicated that known amounts of arsenic (15-15 µg/l) added to these digestion vessels were essentially all recovered from the digestion process (mean of three recoveries = 94 ± 15%).

For arsenic measurements, a Perkin-Elmer Model 305B atomic absorption spectrophotometer equipped with a simultaneous Deuterium Arc Background Corrector, an arsenic Electrodeless Discharge Lamp (EDL), an HGA-2100 Graphite Furnace and a Model 056 recorder was used.

Using 100-µl injections, the working detection limit at 30X scale expansion was ~0.2 µg/l. Unless stated otherwise, normal settings used were the 193.7-nm arsenic analytical wavelength, a spectral bandpass of 0.7 nm, simultaneous deuterium arc background correction, and furnace settings of 2800°C, 8-sec atomization; 175°C, 30-sec charring; 150°C, 40-sec drying; and argon gas interrupt. A hydrogen hollow cathode lamp (Orion) was employed for some of the broadband background absorption measurements.

Confirmatory measurements of arsenic at 193.7 nm were made by the arsine hydride method (5) with a Perkin-Elmer Model 403 atomic absorption spectrophotometer, a Model 056 recorder and an arsine gas generation cell (6).

For calibration of both methods, standard amounts of As_2O_3 were added to deionized water and samples; all were acidified to 0.2% v/v HNO_3.

Using the 251.6-nm wavelength, background correction and a spectral bandpass of 0.2 nm, total silica was measured by direct injection of the homogenized acidified samples into the Graphite Furnace with settings of 2800°C, 8-sec atomization; 1500°C, 25-sec charring and 150°C, 40-sec drying.

*Mention of trade names does not constitute endorsement by the U.S. Environmental Protection Agency.

RESULTS AND DISCUSSION

Problem Description

In support of studies of trace contaminants in natural waters, preliminary investigations were undertaken to determine the applicability of furnace atomic absorption to the determination of arsenic in various types of baseline samples. One water sample type encountered (taken from the mouth of the Ontonagon River, Ontonagon, Michigan on Lake Superior) was particularly high in inorganic particulates (turbidity = 110 NTU). Previous studies on Lake Superior sediments made near that area (7) suggested the presence of a variety of possible silicate mineral types. Measurements of total arsenic in the homogenized, unfiltered, acidified sample gave a value of 13 µg/l, strikingly different from 0.8 µg/l for this same sample after filtration (0.1 µ, Millipore) and acidification. In addition, all other total arsenic concentrations measured for approximately six other streams along Lake Superior's south shore were ≤1 µg/l and were also visibly much lower in turbidity. Despite the fact that normal-shaped and quite reproducible atomization signals were obtained for the Ontonagon sample, it was possible that an interference could be operative.

Spectral Investigation

In pursuing this investigation, measurements of broadband or molecular absorption were made on the Ontonagon sample with a hydrogen hollow cathode lamp in the double-beam mode, in addition to observing the apparent arsenic signal using the EDL, with and without deuterium arc background correction. Both measurements indicated the presence of absorbing molecular species equivalent to ~0.3 absorbance units, well within a range to be compensated for by the instrument's background correction process. In addition, the use of the method of standard additions for calibration indicated no severe signal depression or enhancement as compared to responses from acidified deionized water standards (sensitivity = 13 µg/0.0044 Abs). These two facts narrowed the possibility to a spectral interference.

Since this type of interference is a more difficult type to recognize, several different experiments were conducted to help confirm or deny a problem. The bandpass was varied as indicated in Table I. Both the Ontonagon sample and an arsenic standard (10 µg/l) were injected into the furnace, and the ratios of sample to standard peak heights were calculated for each case. Essentially no change in peak height of the 10 µg/l standard was observed, but a pronounced decrease in the calculated ratio occurred with a decrease in bandpass. This was direct evidence that a spectral interference was present. Since examination of standard wavelength tables (8) revealed no potentially spectrally interfering element, it was likely that the interference could be largely characterized as a molecular spectral interference. In addition, arsenic measurements made at the less sensitive 197.3 nm arsenic wavelength indicated the absence of a major spectral interference since only a small peak height response equivalent to <3 µg/l was obtained for the sample.

TABLE I

Effect of Spectral Bandpass on Apparent Arsenic Response of a River Water Sample[a] High in Particulates

Bandpass (nm)	Relative Response[b]
2.0 (5)[c]	1.4
0.7 (4)	1.1
0.2 (3)	0.6

a. Ontonagon River (mouth), Ontonagon, Michigan.
b. Average peak heights of (sample)/(10 µg/l As standard) at specified bandpass.
c. Slit setting in parenthesis.

Interfering Components

The suspended particulate material visibly appeared to be red clay minerals, and its presence in the sample was likely the result of red clay erosion, a common occurrence along part of western Lake Superior's south shore (9). The concentration measurements of total silica in the sample indicated ~50 mg/l, which suggested that silica was a possible component of the interference; normal baseline concentrations tend to be about 50X lower. A previous report (5) indicated that dissolved silicon dioxide can produce a positive interference, so the possibility was checked experimentally (Table II). However, this interference was too small to explain the large interference observed in this work from a natural sample, and it suggested that other constituents in the sample were also involved, such as the minerals listed.

A possible explanation for these observations is that atomization of certain constituents is inefficient, and an atomic-like absorbing molecular species is produced in the furnace. If we assume that production of such a substance is occurring and also assume that silicate minerals are the major source of interference, then direct decomposition of the substance with hydrofluoric acid would be expected to reduce or eliminate the interference. It is also possible that, during the atomization process, fluoride might react with elements comprising the absorbing molecular species and thus possibly change the absorption spectra so that overlap with the arsenic 193.7 nm wavelength is reduced or nonexistent.

TABLE II

Apparent Arsenic Concentration in Suspensions of Various Silicate Minerals and Dissolved SiO_2 in Dilute Nitric Acid

Constituent	Apparent Arsenic Concentration (µg/l)[a]
Calcium Montmorillonite (250 mg/l) $[(Al, Mg, Fe^{3+})_2 (Si, Al)_4 O_{10} (OH)_2 (Ca)]$	17
Sodium Montmorillonite (250 mg/l) $[(Al, Mg, Fe^{3+})_2 (Si, Al)_4 O_{10} (OH)_2 (Na)]$	19
Kaolinite (250 mg/l) $[Al_2 Si_2 O_5 (OH)_4]$	90
SiO_2 (100 mg/l)	8
0.2% v/v HNO_3	<0.3

a. Spectral bandpass used in measurement was 2.0 nm.

Table III displays examples of data addressing these possibilities. In this experiment concentrations of hydrofluoric acid were added to both the Ontonagon sample and

TABLE III
Effect of Hydrofluoric Acid Concentration On Apparent Arsenic Concentration of a River Water Sample[a] High in Particulates

Hydrofluoric Acid % (v/v)	Relative Response[b]
0	1.3
0.0035	0.7
0.05	0.4
0.2	0.2
1.0	0.2[c]
3.0	0.2

a. Ontonagon River (mouth), Ontonagon, Mich.
b. Defined as ratio of average peak heights of (Sample)/(10 µg/l as standard) at normal instrument settings with both standard and sample containing 0.2% v/v HNO$_3$ and equal concentrations of HF.
c. Relative response was ≈ 10% lower when using a spectral bandpass of 0.2 nm.

a 10 µg/l arsenic standard, and each was directly injected into the furnace. The enhancement or depression of the arsenic signal in these media was checked and found to be negligible. The ratios of sample to standard peak heights dropped sharply to a minimum after the addition of 0.2% v/v hydrofluoric acid. This result supported the possibility that silica or the particular combination of constituents present in the sample was responsible for formation of spectrally absorbing molecular species.

Confirmatory Methods

To examine the possibility that the conspicuously high sample response was due to arsenic tightly bound in the particulate matter, the sample was pressure digested as previously described and analyzed by both the furnace method and the arsine hydride method. The analytical results for this sample and several other samples that were visibly without turbidity are presented in Table IV. Agreement between analytical methods for undigested samples is generally quite acceptable under these conditions with the exception of the Ontonagon location. For that sample, mean digested values of 2.3 and < 2.5 µg/l were measured with the furnace and arsine hydride methods, respectively. In addition, a mean value of < 0.5 µg/l for the unfiltered acidified Ontonagon sample was obtained by the hydride method. This confirmed the presence of a serious spectral error, and it clearly indicated that the value of 13 µg/l was a gross error.

In investigating the probability that different known forms of pure silicate minerals also interfered in a similar fashion, three different suspensions of powdered mineral, normally used for X-ray diffraction standards, were freshly prepared in acidified, deionized distilled water at a nominal concentration of 250 mg/l and were injected directly into the Graphite Furnace. The arsenic content of these specific samples was not measured by an alternate method; however, the apparent concentrations shown in Table II are unreasonably high. Also, when variations of spectral bandpass and hydrofluoric acid concentration were performed on these synthetic samples the relative changes in apparent arsenic concentrations were very similar to those observed for the Ontonagon sample. An exception was that little or no response change was observed for the SiO_2 solution as a function of bandpass.

Since this initial investigation, other natural water samples, visibly high in clay turbidity, have been obtained from two other streams along western Lake Superior's south shore and analyzed. In each case this type of interference was present to the degree that it seriously interfered with the analysis as evidenced by results of tests that have been described above.

TABLE IV
Comparison of Arsenic Concentrations in Natural Water Samples Determined by Graphite Furnace (A) and Arsine (B) Analysis Methods

Sample	Arsenic Concentration (µg/l)[a] Method A	Method B
Lake Superior, Duluth 10/75, unfiltered, undigested	0.7	0.6
Lake Superior, Isle Royale 7/75, unfiltered, undigested	0.8	0.7
Tahquamenon River, Lake Superior 7/75, unfiltered, undigested	1.3	1.0
Tawas River, Lake Huron 6/75, unfiltered, undigested	1.4	1.1
Lake Superior, Ontonagon 7/75, unfiltered, undigested	0.9	0.7
Saginaw River, Lake Huron 7/75, unfiltered, undigested	5.6	6.4
Saginaw Bay, Lake Huron 7/75, unfiltered, undigested	0.7	0.8
Ontonagon River, Lake Superior 7/75, unfiltered, undigested	13.2	< 0.5
Ontonagon River, Lake Superior 7/75, unfiltered, undigested	2.3	< 2.5[b]
Black River, Lake Superior 7/75, unfiltered, undigested	1.2	< 0.5
Thunder Bay River, Lake Superior 6/75, unfiltered, undigested	1.0	0.6
Lake Huron, Cheboygan 6/75, unfiltered, undigested	1.1	0.5

a. Working detection limits were: Method A = 0.5 µg/l, Method B = 0.5 ng/l.
b. Sample diluted by five before analysis.

CONCLUSION

Serious molecular spectral interferences may occur in furnace atomic absorption determinations of arsenic in natural water samples containing relatively low arsenic concentrations and high concentrations of suspended silicate minerals. The addition of hydrofluoric acid to the sample and the use of a narrow bandpass will help control and identify this problem. Use of the less sensitive 197.2-nm analytical wavelength is an additional alternative; however, it was not tested here for routine use. The furnace method can be very valuable for baseline natural water analysis, (e.g. Lake Superior water), but the method must be used judiciously. More research is needed to determine the degree and manner of interference by other substances.

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